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POTASSIUM ISOTOPE COSMOCHEMISTRY, VOLATILE DEPLETION AND THE ORIGIN OF THE EARTH; M. Humayun<sup>1</sup> and R. N. Clayton<sup>1,2</sup>, <sup>1</sup>Dept. of Geophysical Sciences, <sup>2</sup>Enrico Fermi Institute and Dept. of Chemistry, University of Chicago, Chicago, IL 60637, USA.

We report the first results obtained by our techniques for the precise and accurate determination of the isotopic composition of potassium [1] to constrain the mechanism of volatile element depletion in the formation of the Earth, Moon and meteorites. Our measurements of  $\delta^{41}\text{K}$  for six chondrites and ten terrestrial rocks attained an average precision of the individual measurement of  $\pm 0.4\text{‰}$  ( $2\sigma$ ;  $\pm 0.2\text{‰}$  a.m.u.) and yield a net chondrite-Earth difference unresolved at the 99% confidence limit,  $\Delta^{41}\text{K} = -0.32 \pm 0.35\text{‰}$  ( $3\sigma$ ). This sets a firm upper limit of  $1.3 \pm 1.4\%$  Rayleigh evaporation of terrestrial potassium (using  $\alpha = \sqrt{41/39}$ ), compared with an observed  $\approx 85\%$  chemical depletion of K relative to C1 chondrites. Similar conclusions are reached for the SNC meteorites, Shergotty and Zagami, for 15495 (lunar mare gabbro), and for the eucrite Juvinas. Our conclusion is that direct evaporation of volatile elements from planets (e.g. from silicate vapor atmospheres following giant impact [2]) can be ruled out, and the cause of volatile loss must be sought elsewhere, e.g. nebular processes [3]. Our present findings do not support the conclusions of Hinton *et al.* [4,5], the discrepancy to be resolved at a later date. We also find lunar soil 64801,  $\delta^{41}\text{K} = +4.99 \pm 0.53\text{‰}$ , to be distinctly heavy in accord with Garner *et al.* [6].

Planets and planetesimals have been subjected to high temperature processing evidenced by the systematically lower abundances of volatile elements compared with Mg, Si, and Fe, and a complementary enrichment of refractory elements [3]. Recent models of planetary accretion have emphasized the role of large impacts in planetary growth, and volatile element depletion has been proposed as a cosmochemical signature of vaporization accompanying such impacts [2]. Volatile element depletion has previously been attributed to nebular processes, e.g. incomplete condensation. The processes of partial evaporation can be distinguished from incomplete condensation by the production of large mass-dependent isotopic fractionation (Rayleigh distillation) in elements that otherwise lack stable isotopic variations in nature. It has been our ambition to determine which of these processes was principally active in the formation of planets by searching for such isotopic fractionation in bulk planetary compositions. Candidate elements must be moderately volatile, preferably light in mass, and not be subject to equilibrium or kinetic isotopic effects due to geological processes (e.g. Li, B, Cl, S). Additionally, incompatible lithophile elements are preferable to chalcophile elements as the extent of lithophile element depletion is easily ascertainable from volatile/refractory ratios (K/La, K/U, Rb/Sr, Cs/Ba, etc.). This is a very restrictive criterion, and would not be satisfied by any element if we required that the element be conveniently determined by routine mass spectrometric techniques. The choice of K over Rb and Zn is obvious, and a suitable mass spectrometric procedure had to be developed. An early attempt utilizing ion microprobe measurements of K-rich minerals indicated some interesting results [4,5] but was limited in scope by both the rarity of suitable minerals in chondrites, and by the ability to convincingly demonstrate the precision and accuracy of the ion probe technique.

**Experimental Techniques:** We have previously detailed most of our experimental techniques [1]. We separate K by ion exchange and mount it in 2% K Ba-borate glass prepared by fusion from Suprapur<sup>®</sup> reagent  $\text{Ba}(\text{NO}_3)_2$  and  $\text{H}_3\text{BO}_3$ . Six sample beads are mounted on a glass slide with an equal number of standard beads, prepared from Suprapur<sup>®</sup>  $\text{KNO}_3$  (our in-house standard). The K isotopes, 39 and 41, are measured using the Chicago AEI IM-20 ion microprobe at  $M/\Delta M \approx 300$ . All instrumental tunings are set at the beginning of each day, except repeller and MS7 Z focus controls, which are tuned separately for each point to give maximum intensity. Isotopic ratios are found to be independent of the applied voltage settings. Internal precision of a single point is  $\approx \pm 1\text{‰}$  ( $\pm 0.75\text{‰}$  counting statistics), and external precision of a block of 10 to 16 points is  $\approx \pm 0.6\text{‰}$ . Instrumental fractionation is removed by determining the isotopic difference between the sample and the standard, with error propagation,

$$\delta^{41}\text{K} = [(41/39)_x / (41/39)_{\text{std}} - 1] \times 1000 \pm 2\sigma_N, \text{ and}$$

$$\Delta^{41}\text{K} = \delta^{41}\text{K}_A - \delta^{41}\text{K}_{\text{Earth}} \pm \{(3\sigma_A)^2 + (3\sigma_{\text{Earth}})^2\}^{1/2}$$

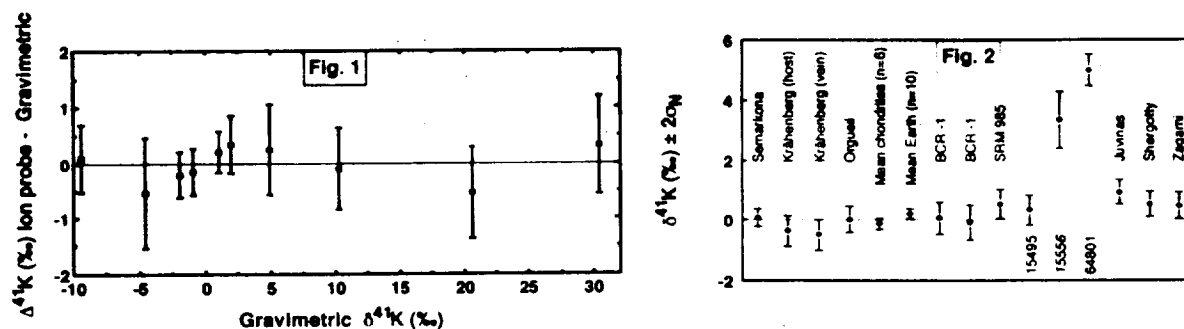
The precision obtained is in large part due to the good point to point reproducibility of the K secondary ion intensity, and the ability to alternate standard and unknown points on the same thin section, with equivalent tuning adjustments. To demonstrate both precision and accuracy, we prepared enriched

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standards in the range -10 to +30 ‰ using ORNL separated isotopes, the results of which are shown in Fig. 1, and obtain good agreement between gravimetric and ion probe determined  $\delta^{41}\text{K}$ . Fractionation during ion exchange chromatographic separation is limited by effectively complete recovery of K from the column (> 99.8 %). This is hardest to obtain for samples with low K and high Mg contents where recovery is  $\approx 97$  %. Blank contributions of K are kept below  $10^{-3}$ .

Results (a selection of which is shown in Fig. 2) obtained on ten terrestrial samples spanning a wide compositional range indicate that individual measurements of  $\delta^{41}\text{K}$  do not deviate by more than the mass spectrometric error from the terrestrial mean. A similar result can be obtained by comparing the six measurements on L and LL chondrites. Replicate analyses have been carried out on separate aliquots of BCR-1, and on Krähenberg [courtesy H. Palme, 7], with excellent agreement obtained. It can also be seen that the mean of all L/LL chondrites and Orgueil C1 is separated from mean terrestrial K by less than  $3\sigma_{\text{mean}}$ . Similarly, Shergotty, Zagami, and mare gabbro 15495 are within error of terrestrial K. Results for Juvinas, and the CV chondrites Leoville and Vigarano differ by  $\geq 4\sigma$ , which we are cautious to interpret as intrinsic fractionations, given that all the distinct samples share the lowest recovery obtained. Further experiments are being carried out on separated components of CV chondrites. Lunar soil 64801 is distinctly heavier,  $\delta^{41}\text{K} = +4.99 \pm 0.53$  ‰, and our values for 64801 and 15495 agree within error with [6]. The value of 15556 mare basalt is being redetermined, and additional measurements of lunar mare basalts and highlands samples are in progress.

**Cosmochemical Interpretations:** First we note that our main result, the absence of significant fractionation between chondrites and terrestrial, lunar and achondritic samples based on direct measurement, stands in stark contrast to the observations of Hinton *et al.* [4,5]. Further, the presence of large effects, on the order of the square root of the masses of  $^{41}\text{K}$  and  $^{39}\text{K}$ , is a necessary consequence of any partial evaporation hypothesis for volatile element depletion in planets, e.g. Jeans escape from a silicate vapor atmosphere, where the residual vapor is enriched in the heavy isotope. We note that, although a silicate vapor atmosphere is a likely consequence of any model for the origin of the Earth involving large impacts (including the Moon-forming Giant Impact), such models do not all require that the vapor escape from the Earth's gravity field [8]. Given the large escape velocity of the Earth (11.2 km/s for 1.0 Earth mass), significant escape of vapor species with  $m \approx 40$  a.m.u. only takes place if the silicate vapor atmosphere has an exobase  $T \approx 10^5$  K, compared with model derived surface  $T \approx 10^4$  K. We also observe that such fractionation must have embarrassing chemical implications, because at  $T \approx 10^4$  K the distinction between volatile and refractory elements is lost, as the entire portion of the planet affected will be in the vapor phase. Thermal loss from this phase in a mass dependent manner should significantly deplete *light* species (e.g. Li, Mg, Al) over *heavy* species (e.g. Cs, Yb, Pb). We do not find any support for models [2, 9] that allow thermal vaporization accompanying the Moon-forming giant impact (or impacts) to shape the Earth's chemical characteristics (including the Mg/Si, Fe/Si ratios of the mantle).



- [1] Humayun *et al.* (1991) LPS XXII, 597. [2] Cameron and Benz (1991) Icarus 92, 204. [3] Palme *et al.* (1988) Meteorites and the Early Solar System, Arizona, 436. [4] Hinton *et al.* (1987) LPS XVIII, 429. [5] Hinton *et al.* (1988) LPS XIX, 497. [6] Garner *et al.* (1975) PLSC 6, 1845. [7] Wlotzka *et al.* (1983) GCA 47, 743. [8] Stevenson (1987) Ann. Rev. Earth Planet. Sci. 15, 271. [9] Ringwood (1992) EPSL 111, 537. [10] Taylor (1991) Meteoritics 26, 267-77.